CHAOTIC DYNAMICS IN DENSE FLUIDS

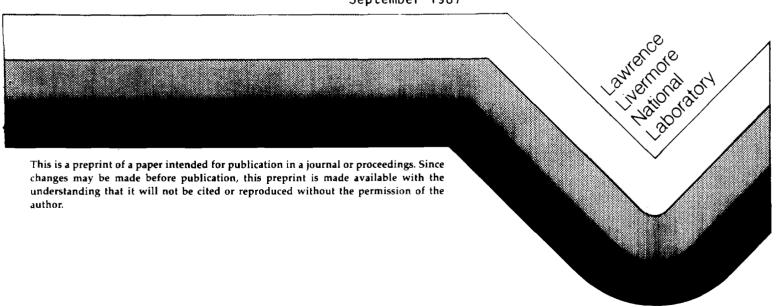
H. A. Posch Institute for Experimental Physics University of Vienna Boltzmanngasse 5, A-1090 Vienna Austria

and

W. G. Hoover Lawrence Livermore National Laboratory University of California Livermore, CA 94550

This paper was prepared for the proceedings of the Physics of Fluids Conference Calibria, Italy--September 22, 1987

September 1987



DISCLAIMER

This document was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor the University of California nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial products, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government thereof, and shall not be used for advertising or product endorsement purposes.

Work performed under the auspices of the U.S. Department of Energy by the Lawrence Livermore National Laboratory under contract number W-7405-ENG-48.

Chaotic dynamics in dense fluids

H.A.Posch and W.G. Hoover *

Institute for Experimental Physics, University of Vienna, Boltzmanngasse 5, A-1090 Vienna, Austria

We present calculations of the full spectra of Lyapunov exponents for 8- and 32-particle systems with periodic boundary conditions and interacting with the repulsive part of a Lennard-Jones potential both in equilibrium and nonequilibrium steady states. Lyapunov characteristic exponents λ_n describe the mean exponential rates of divergence and convergence of neighbouring trajectories in phase-space. They are useful in characterizing the stochastic properties of a dynamical system. A new algorithm for their calculation is presented which incorporates ideas from control theory and constraint nonequilibrium molecular dynamics [1,2].

For the simulations isokinetic equations of motion based on Gauss's principle of least constraint are used, which are a limiting case of the even more general isothermal mechanics invented by S. Nosē. Nonequilibrium steady states are generated by the application of an external field F. through which an equal number of particles are accelerated in opposite directions. In equilibrium with no external field applied $(F_e = 0)$, the Lyapunov spectra are symmetrical around zero and the sum over all exponents vanishes. This is shown in the figure for an equilibrium 32-body fluid (reduced density = 0.5, reduced temperature = 1.0). The smooth line is the fit of a power law, $\lambda = \alpha n^{\beta}$, to the data, where n is the number of positive exponents less or equal to a given value of λ . All quantities are given in reduced units with the Lennard-Jones parameters σ , ϵ and the particle mass m acting as units of length, energy and mass, respectively. We find $\alpha = 0.63$ and $\beta = 0.38$. Such a power law may be derived from the simple Debye model for vibrational frequencies in solids with $\beta_{Debye} = 1/3$. The maximum Lyapunov exponent is also close in value to the Debye frequency.

For nonequilibrium steady states $(F_e \neq 0)$ the Lyapunov spectra are not symmetrical and the sum over all Lyapunov exponents is negative. This means that the distribution function eventually diverges to infinity

^{*} Permanent address: Department of Applied Science, University of California at Davis-Livermore and Lawrence Livermore National Laboratory, University of California, California 94550, USA.

indicating a collapse of the phase-space probability onto a subspace of zero volume. This subspace is a fractal attractor as found previously in simpler systems [3,4]. In these steady-state systems the energy supplied by the external field is continuously dissipated and removed by the thermostat. However, the Gauss and Nosē equations of motion are invariant with respect to time reversal. The only trajectories which could violate the Second Law would have to start on the repeller states obtained from the fractal attractor by a time reversal transformation. Since the repeller is also a fractal with zero volume in phase-space, the probability of such trajectories to occur is zero. Thus Nosē mechanics resolves the old reversibility paradox of Loschmidt for nonequilibrium steady states.

- [1] W. G. Hoover, H. A. Posch and S. Bestiale, "Dense-Fluid Lyapunov Spectra via Nonequilibrium Molecular Dynamics", J. Chem. Phys., submitted, (1987).
- [2] H. A. Posch and W. G. Hoover, "Lyapunov Instability of Dense Lennard-Jones Fluids", in preparation.
- [3] W. G. Hoover, H. A. Posch, B. L. Holian, M. J. Gillan, M. Mareschal, C. Massobrio, and S. Bestiale, "Dissipative irreversibility from Nose's reversible mechanics", Molecular Simulations, in press, (1987).
- [4] B. Moran, W. G. Hoover, and S. Bestiale, "Diffusion in a periodic Lorentz gas", J. Stat. Phys., in press, (1987).

